UDC 666.112.9:66.01:531.424

REACTIONS BETWEEN INGREDIENTS IN BINARY SILICATE GLASSES

V. V. Samoteikin[1] and O. A. Gladushko[1]

It is demonstrated that the density of binary glasses upon variation of the molar content of the modifier in their compositions obeys a parabolic dependence, whose parameters can be used to estimate the extent and type of reactions between the components. The reaction parameters in glasses that are prone to liquation are lower by an order of magnitude and have the negative sign.

Glasses as solids solutions have a structure that depends on the type of reactions between its components. As glass structure determines the macroscopic properties of glass, in a certain approach these properties can be a key to information regarding reactions between the components. The property considered in the present study is the density of binary glasses depending on glass composition.

This relationship is known to be complex: for some glasses it can be represented as a smooth curve with a positive or negative curvature within the total range of known compositions, in other glasses the curve can have break points and segments with different curvature signs, the positive curvature indicating a tendency for stratification of glass and the negative curvature found in glasses with a homogenous composition [1].

The present study suggests an approach whereby one can estimate the level and type of reactions between components based on the parameter values of the analytical dependence of glass density on its composition.

The dependence of binary glass density on the molar content of the modifier component will be described here using the principle according to which glass density is made up of the partial densities of its components and the term responsible for their interactions:

$$\rho = \rho_A (1 - x) + \rho_B x + \rho_{AB} x (1 - x), \qquad (1)$$

where ρ, ρ_A, and ρ_B are the mean density and the densities of components A and B, respectively; ρ_{AB} is the index of the component interaction; x is the molar content of component B in a glass of composition $x_B - (1 - x)_A$.

The emergence of the third summand in expression (1) means that deviation of the relationship $\rho(x)$ from the linear law is related to variations in the parameters of the compo-

nent structure: consolidation of the structure if $\rho_{AB} > 0$, or its loosening if $\rho_{AB} < 0$. Therefore, the presence of the third summand in this dependence is an indicator of the mutual effect of the components. The choice of this summand implies proportionality of the mutual reaction effect to the molar contents of the reaction components. This is substantiated by an experimental fact, namely, that all glasses yield good results when parabolic smoothing is applied to the smooth segment of dependence $\rho(x)$:

$$\rho = c + bx + ax^2. \qquad (2)$$

The parameter values in the above equation are related to the properties of glass components:

$$c = \rho_A; \quad b = \rho_B - \rho_A + \rho_{AB}; \quad a = -\rho_{AB} \qquad (3)$$

and are found from experimental points by the least squares method [2].

It can be see from Figs. 1 and 2 that the curves correlate with parabolic dependence (2) whose parameter values are given in Table 1. The parameter c in all silicate glasses correlates with the melted silica density $\rho_A = 2.2$ g/cm³. The curve segment located within the composition range, based on which the values of parameters a and b are determined, is indicated by a solid line and extrapolation of dependence (2) beyond this range is indicated by a dashed line.

The curves in Fig. 2 are constructed in reduced coordinates $x' = x/x_2$, i.e., depending on the molar content of component B′, which can represent a combination of the initial components A and B. These coordinates for potassium-silicate and borosilicate glasses coincide with a molar content of the respective oxide, and for sodium-silicate and lithium-silicate glasses yield a molar content value of the respective silicate: $Na_2O - 4SiO_2$ and $Li_2O - 2SiO_2$.

---

[1] Moscow State Metallurgy Night Institute, Moscow, Russia; Institute of Glass Joint-Stock Company, Moscow, Russia.
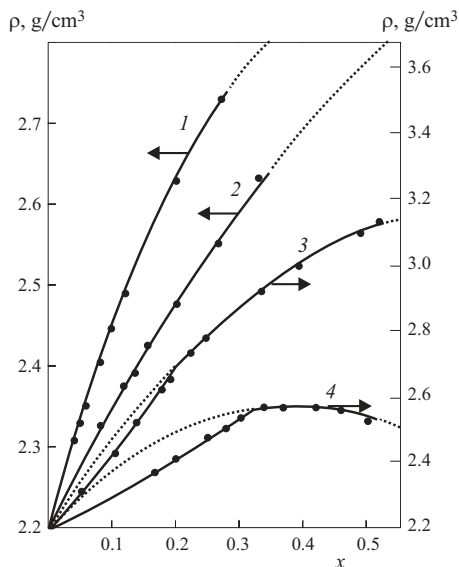
Fig. 1. Results of parabolic smoothing of the dependence of alkali-silicate glass density on the molar content of oxide based on experimental data in [3]. Modifiers: *1*) Cs (Yu. A. Shmidt and Z. D. Alekseeva); *2*) Rb (Yu. A. Shmidt and Z. D. Alekseeva); *3*) Na (G. V. Morey); *4*) Li (S. K. Dubrovo and Yu. A. Shmidt).

It can be seen that the composition range used to identify the smoothing parameters is a smaller part of the total range of possible composition variations. Accordingly, the result of

extrapolation of dependence (2) to $x = 1$ ought to strongly depend on experimental results on the parameter identification segment. Figure 2 shows the results of extrapolation for potassium-silicate glasses based on data published by different authors. However divergence at the point $x = 1$ does not exceed 3%.

The authors and results of respective measurements are cited from a reference book [3]. Preference was given to authors who investigated properties of silicate glasses with various modifiers in a wide range of compositions. All data were registered at room temperature.

The densities of crystalline oxides are cited from two sources: data in round brackets are from reference book [6] and data in square brackets are either taken directly from [5] or calculated on the basis of data from that source.

The "component B" column indicates the formulas of a compound correlating to the value of density in the amorphous state listed in the column "ρ_B." These values are the results of extrapolation of dependence (2) to $x = 1$. For reference purposes, the column "ρ_B of crystalline modification" shows the density values of these compounds in the crystalline state. The column "application range" shows boundaries of the molar content of component B for which the parameter values in dependence (2) are true.

It can be seen from relationships (3) that along with the reaction indicator ρ_{AB}, parameter a determining the curva-

TABLE 1

Component B	Application range	a, g/cm³	ρ_{AB}, g/cm³	b, g/cm³	ρ_B, g/cm³	ρ_B of crystalline modification, g/cm³	Experimental data from [3]
Li_2O	$0.333 - 1$	-0.983	0.980	0.770	1.987	[2.04] (2.01)	S. K. Dubrovo and Yu. A. Shmidt[*]
$Li_2O - 2SiO_2$	$0 - 0.333$	0.222	-0.025	0.368	2.347	$-$	
Na_2O	$0.2 - 1$	-0.877	0.880	1.175	2.498	[2.41][**] (2.27)	G. V. Morey
$Na_2O - 4SiO_2$	$0 - 0.2$	0.281	-0.013	0.906	2.390	$-$	
K_2O	$0 - 1$	-1.043	1.040	1.165	2.322	[2.36][**] (2.32)	Yu. A. Shmidt,[***] Z. D. Alekseeva, and R. J. Charles
		-1.080	1.080	1.140	2.260		
Rb_2O	$0 - 1$	-1.903	1.900	3.851	4.148	[4.06][**] (3.72)	Yu. A. Shmidt and Z. D. Alekseeva
Cs_2O	$0 - 1$	-4.250	4.250	6.390	4.340	[4.68] (4.36)	Yu. A. Shmidt[****] and Z. D. Alekseeva
CaO	$0 - 1$	-0.551	0.550	1.657	3.306	[3.38][**] (3.4)	G. V. Morey and M. Schwartz
PbO	$0 - 1$	1.300	-1.300	6.840	10.340	[9.34][**] (9.51)	R. R. Show and D. R. Ulman
B_2O_3	$0 - 1$	0.148	-0.150	-0.512	1.836 (1.840)	[1.818] (2.46)	R. Bruckner and I. F. Navarro

[*] The result given for $x = 0.5$ disagrees with a smooth dependence and was neglected in parabolic smoothing.

[**] Calculated from the molar volume value given in [5].

[***] The result given for $x = 0.417$ disagrees with a smooth dependence and was neglected in parabolic smoothing.

[****] Parabolic smoothing took into account the value of the crystalline oxide density from [4].

ture value and sign of the dependence $\rho(x)$ can be regarded as a measure of reactions between the components.

Expression (1) implies that at the range boundaries, where properties are determined by reaction between components A and B, the density coincides with the density of component A or component B. If not all points in the composition range considered satisfy the parameters of dependence (2), i.e., a curve consists of several smooth segments, this means that the composition of reactant components changes from one segment to another, and for different segments one should consider reactions between different components. For instance, the new component B′ correlates with the composition $x_{2B}(1 - x_2)_A$ of the original components A and B and, accordingly, we are interested in the parameters of reactions between components A and B′. Consequently, the composition variation interval is narrowed to a range limited by components A and B′: $0 \leq x \leq x_2$, but the variation range of the new component B′ in glass compositions $x'_{B'} - (1 - x')_A$ will encompass an interval from 0 to 1. In this case expression (1) should be written with new variables:.

$$\rho = \rho_A(1 - x') + \rho_{B'} x' + \rho_{AB'} x'(1 - x'),$$

where $x' = x/x_2$.

In this case the parabolic smoothing parameters obtained for variable x from expression (3) will be related to the parameters of equation (2) in the variable reduced x' via a dependence:

$$a' = ax_2^2, \quad b' = bx_2.$$

The value of the parameter c in this case does not vary, but the reaction index is related precisely to the value a'.

If, starting with a certain composition $x_{1B}(1 - x_1)_A$, the component A′ is a new one, and the old component B does not change, the new variable satisfies the condition

$$x' = \frac{x - x_1}{1 - x_1},$$

and the new parameters are related to the old relationships:

$$a' = a(1 - x_1)^2; \quad b' = (1 - x_1)(b + 2ax_1); \quad c' = c + bx_1 + ax_1^2.$$

Summing over partial densities yields the value of the density of material, if there is no difference in reactions between homogeneous and heterogeneous components. This means that the volume part of each component coincides with its molar content x in glass (similarly to the behavior of components in a mixture of ideal gases). If such difference exists, the equality is disturbed: with a negative ρ_{AB} the glass loosens, and with a positive value it consolidates. All known data show that consolidated glasses have a homogenous composition, i.e., reactions between heterogeneous components are more intense than between homogenous compo-
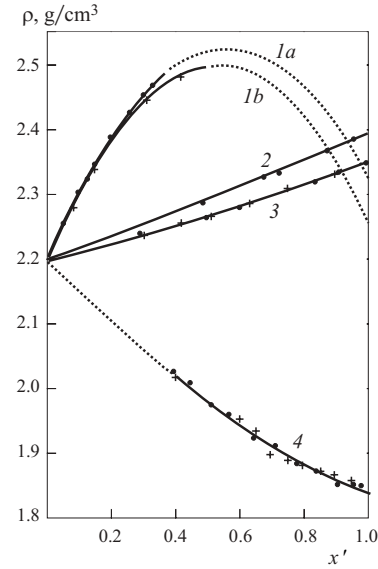

Fig. 2. Results of parabolic smoothing of the dependence of silicate glass density on the molar content of component B′: *1a*) K_2O (Yu. A. Shmidt and Z. D. Alekseeva [3]); *1b*) K_2O (R. J. Charles [3]), *2*) $Na_2O - 4SiO_2$ (G. V. Morey [3]); *3*) "+" (S. K. Dubrovo and Yu. A. Shmidt [3]); "●" (Yu. N. Kondratiev and L. A. Smirnova [3]); *4*) B_2O_3 "●" (R. Bruckner, I. F. Navarro [3]); "+") M. Imaoka, H. Hacegawa [4]).

nents. Otherwise there is a tendency to stratification: each component tends to unite with a similar one, and heterogeneity areas are formed in glass. Thus, the parameter ρ_{AB} reflects a relative value of interaction between homogeneous and heterogeneous components.

In the case of glasses with a heterogeneous structure, when interaction between heterogeneous components is low compared to reactions between homogeneous components, it is possible to speak of the existence of two phases, andminstead of expression (1) one can write

$$\rho\varphi = \rho_1 \varphi_1 + \rho_2 \varphi_2 = \rho_1(1 - \varphi_2) + \rho_2 \varphi_2, \quad (4)$$

where φ_1 and φ_2 are the volume parts of the first and the second phases, respectively: it is taken into account that $\varphi = \varphi_1 + \varphi_2 = 1$.

If z_1 and z_2 are the numbers of moles of the respective phases in a considered volume, the total number of moles of component $B(xz)$ satisfies the condition

$$xz = x_1 z_1 + x_2 z_2,$$

where x_i is the molar content of component B in the ith phase.

Considering that $z = z_1 + z_2$, we get the "lever rule":

$$z_1(x - x_1) = z_2(x_2 - x). \quad (5)$$

TABLE 2

Second phase composition	x_2	ρ_2, g/cm³	k	a, g/cm³	b, g/cm³
$Li_2O - 2SiO_2$	0.333	2.347	1.28	0.22	0.35
$Na_2O - 4SiO_2$	0.200	2.391	1.08	0.32	0.88
B_2O_3	1.000	1.840	0.72	0.19	− 0.50
PbO	1.000	10.340	1.18	1.05	6.90

Representing z_1 and z_2 via the volume parts of each phase ($z_i = \varphi_i \rho_i / M_i$), instead of expression (5) we obtain

$$\varphi_1 (x - x_1) = \varphi_2 k (x_2 - x), \qquad (6)$$

where $k = \dfrac{M_1 \rho_2}{M_2 \rho_1}$ is the ratio of the molar volumes of the first and the second phases (M_i is the molar mass of the respective phase: $M_i = M_A + x_i (M_B - M_A)$).

Using Eqs. (4) and (6), we get

$$\rho = \rho_1 + \frac{(\rho_2 - \rho_1)(x - x_1)}{kx_2 - x_1 - x(k - 1)}. \qquad (7)$$

If $k = 1$, then $\rho = \rho_1 + b_0 (x - x_1)$ and relationship $\rho(x)$ is linear:

$$b_0 = \frac{\Delta\rho}{\Delta x}, \quad \Delta x = x_2 - x_1, \quad \Delta\rho = \rho_2 - \rho_1.$$

The values calculated based on expression (7) agree well with experimental data. Therefore, along with formula (1), it can be considered as another analytical method for representing the dependence $\rho(x)$ in the range of compositions with a heterogeneous structure. Correlation of expressions (1) and (7) makes it possible to identify a relationship between the reaction index ρ_{AB} and the macroscopic parameters of the reactant phases.

Decomposing expression (7) into a series $x - x_1$ and limiting ourselves to quadratic terms, we represent formula (7) as a square trinomial (2) with the parameters

$$b = \frac{b_0}{k}; \quad a = \frac{b(k - 1)}{\Delta xk}; \quad c = \rho_1. \qquad (8)$$

Thus, using Eqs. (8), the parameters ρ_{AB} is expressed via the difference between the densities of the reactant phases ($\rho_2 - \rho_1$) and the ratio of their molar volumes k. The size of the range $x_2 - x_1$ is not significant, since $\rho_{AB} = - a' = - a\Delta x^2 = \Delta\rho (1 - k)/k^2$ and does not depend on it.

Despite the errors of such decomposition, the parameter values calculated from formulas (8) and listed in Table 2 satisfactorily agree with values obtained as a result of parabolic smoothing of the experimental dependence (Table 1).

Since the parameter a determines the curvature sign, it is easy to verify that the following condition is the criterion of its positiveness:

$$\rho_2 > \rho_1, \quad k > 1;$$

$$\rho_2 < \rho_1, \quad k < 1.$$

Table 2 shows data corroborating the appropriateness of this criterion, using as example silicate glasses with known values of boundary compositions of the stratification area. It is assumed that the lower composition boundary corresponds to pure silica, i.e., $x_1 = 0$, $\rho_1 = 2.2$ g/cm³.

Analysis of the parameters of parabolic smoothing of dependences listed in Table 1 suggests the following.

Considering the reactions between such glass components as silica and the modifier oxide, the reaction index in all alkali-silicate glasses varies approximately 4 times and grows with increasing atomic number of the modifier. The sign of ρ_{AB} points to the prevailing role of reactions between heterogeneous components in the formation of glass structure.

In glasses prone to liquation the reaction indexes are lower by an order of magnitude and negative.

REFERENCES

1. R. R. Shaw and D. R. Uhlman, "Effect of phase separation of the properties of simple glasses," *J. Non-Cryst. Sol.*, **5**(3), 237 – 263 (1971).
2. I. N. Bronshtein and K. A. Semendyaev, A *Mathematics Handbook* [in Russian], Nauka, Moscow (1980).
3. O. A. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskya, *Properties of Glass and Glass-Forming Melts, A Handbook, Vol. 1* [in Russian], Nauka, Leningrad (1973).
4. O. A. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskya, *Properties of Glass and Glass-Forming Melts, A Handbook. Vol. 4, Part 1* [in Russian], Nauka, Leningrad (1980).
5. B. F. Ormont, *Structures of Inorganic Materials* [Russian translation], Gosizdat, Moscow – Leningrad (1950).
6. A. I. Efimov, L. P. Belorukova, I. R Vasil'eva, et al., *Properties of Inorganic Compounds, A Handbook* [in Russian], Khimiya, Leningrad (1983).